Electrical Conduction in Trivalent Chromium and Nickel Molybdate

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The electrical conductivity (σ) and Seebeck coefficient (S) of trivalent chromium and nickel molybdate are measured at 500–1200 K. On the basis of these data it is concluded that chromium molybdate undergoes a phase transition at 780 K and nickel molybdate at 740 K. log σ and S depend linearly on T^{-1} in certain temperature ranges. It is shown that the conduction mechanism in these solids is essentially of the band type in which the O^{2-}:2p band is the valence band and M^{3+}:4s (transition metal 4s band) the conduction band. Under simplifying assumptions the energy band gap and the mobility of the charge carriers are evaluated.

1. Introduction

Trivalent molybdates of 3d-elements were synthesized for the first time by Nassau et al. [1] who reported that not all 3d-elements form trivalent molybdates. Else very little [2–4] is known about these compounds. This prompted us to investigate the magnetic and electrical transport properties of all possible molybdates of 3d-elements. Some of our studies in this direction have already been published [5–8]. In this paper we report the electrical conductivity (σ) and the Seebeck coefficient (S) of Cr and Ni molybdate. These molybdates are orthorhombic with unit cell parameters at room temperature as given in Table 1 [1, 8].

2. Material Preparation and Experimental Technique

The starting materials for the preparation of the molybdates were Ni_2O_3 and Cr_2O_3 from Rare and Research Chemicals, India, and MoO_3 from Bonds, India, all stated purity of 99.99%. After having been dried at 500 K, the stoichiometric amounts of these materials were thoroughly mixed, made into pellets and fired in air for 24 hours in a platinum crucible at 700 K for chromium and 600 K for nickel molybdate. The reaction product was again ground, made into pellets and fired at 800 K for more than 24 hours. This process was found sufficient for the formation of a single phase compound. The details of pellet preparation, electrode making and measuring techniques were same as those described in [9, 10].

3. Results and Discussion

In the measurement of σ and S it is essential to have ohmic contact at the electrodes [11]. We have used platinum foils (thickness $\simeq$ 0.02 mm) pressed mechanically on the pellet faces. The ohmic contact was confirmed by the linear current-dc voltage plot obtained. The current at constant temperature and dc voltage was almost independent of time, indicating that the current in these solids is electronic.

Air pores and grain boundaries, which have a significant effect on the values of σ and S, can not be avoided in pellets but they can be significantly reduced by using highly pressed pellets. Our pellets were made of fine and uniform grain powders at pressures exceeding 8×10^8 N m^{-2} and sintered in

Table 1. Structural parameters of the studied orthorhombic molybdates.

	Lattice parameters			References
	a_0 nm	b_0 nm	c_0 nm	
$Cr_2(MoO_4)_3$	0.910	0.912	1.260	[1]
$Ni_2(MoO_4)_3$	0.806	0.807	1.204	[8]

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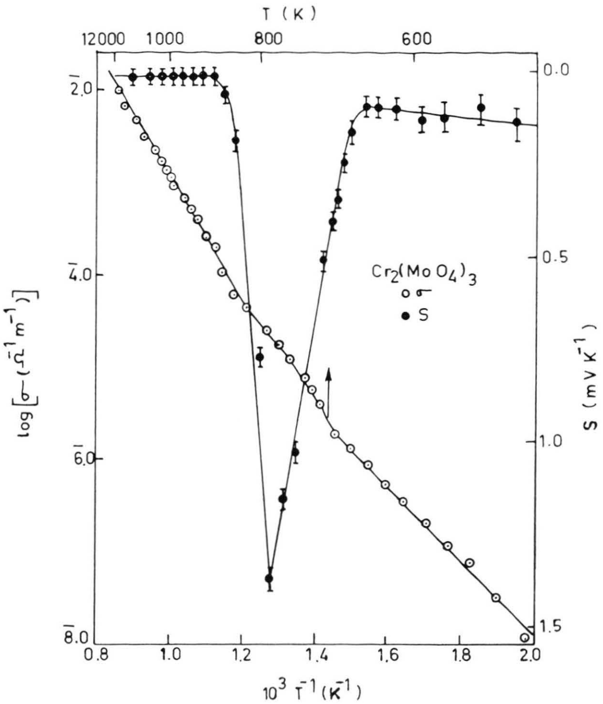

Fig. 1. Plot of logarithm of electrical conductivity (log σ) and Seebeck coefficient (S) against inverse of absolute temperature (T) for chromium molybdate.

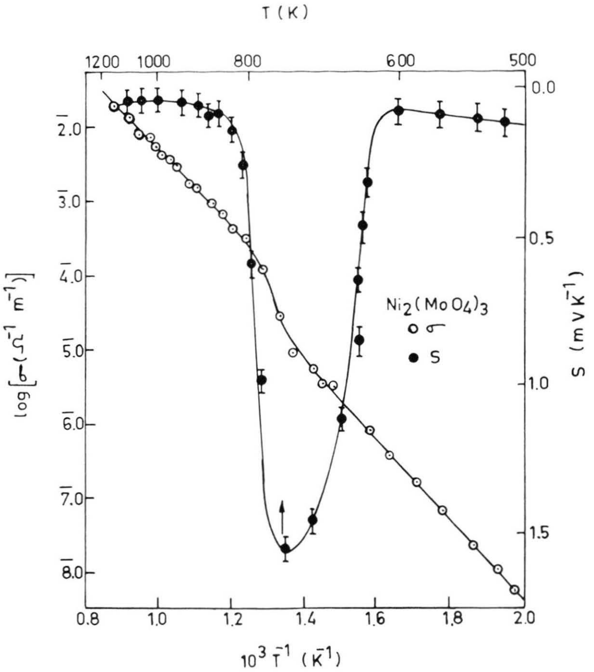

Fig. 2. Plot of logarithm of electrical conductivity (log σ) and Seebeck coefficient (S) against inverse of absolute temperature (T) for nickel molybdate.

air at 700 K for two days. Pellets of different dimensions yielded almost the same values of σ and S. σ has also been found independent of ac frequency (0 to 10^4 Hz). The independence of σ from the pellet dimensions, pelletizing pressure and signal frequency indicates that our values of σ represent the bulk values, grain boundary effects being minimum. The σ values have been corrected for voids using a relation given in [12].

Our final values of σ and S are averages of values obtained with different pellets. The latter did not differ considerably. Figures 1 and 2 show the plots of log σ and S vs. T^{-1} for Cr and Ni molybdate, respectively. Below 500 K σ becomes too small to be measured. The σ plots show two linear regions, which can be represented by the relation

$$\sigma = \sigma_0 \exp(-E_a/kT)\,. \tag{1}$$

The values of σ_0 and E_a for the different regions are given in Table 2. The log σ vs T^{-1} plots show a break at a temperature (T_B). The S values could not be measured below 500 K due to the high resistance of the samples. S varies linearly with T^{-1} up to a certain temperature where it shows a sudden drop. After having again risen steeply it becomes constant in the temperature ranges 890 – 1200 K and 850 – 1200 K for Cr and Ni molybdate respectively. The sign of S remains negative throughout the measured temperature range, indicating positive charge carriers according to our convention. The linear parts of the S vs. T^{-1} plot can be represented by the equation

$$S = \eta/eT + H\,. \tag{2}$$

The values of the slope η and intercept H for the different regions are also given in Table 2.

We have tried to explain our data with a simple energy band model. The relevant electron energy bands which may be important in these solids are O^{2-}:2p, M^{3+}:3d, M^{3+}:4s and Mo^{6+}:4d in order of increasing energy. The last two bands are empty and the M^{3+}:3d band is partially filled. Thus according to band theory these molybdates should be metallic. But they are almost insulators. It can,

Table 2. Summarized results of σ and S measurements.

σ measurement			S measurement				
Temp. range (K)	E_a (eV)	σ_0 (Ω^{-1} m^{-1})	Temp. range (K)	η (eV)	H (mV K^{-1})	T'_B (K)	Charge carrier
			$Cr_2(MoO_4)_3$				
500– 695	1.07	4.15×10^2	500– 690	−0.12	+0.09	780	h
820–1200	1.28	3.09×10^4	820–1200	−0.02	−0.02	–	h
			$Ni_2(MoO_4)_3$				
500– 690	1.05	1.64×10^2	500– 625	−0.10	+0.10	740	h
800–1200	1.28	6.31×10^3	850–1200	−0.02	−0.02	–	h

therefore, be concluded that the M^{3+}:3d band is narrow and unable to support metallic conduction. Hence these 3d electrons either do not take part in the electrical conduction, or if they do so, it is through a low mobility small polaron (localized electrons in a 3d band behave as small polarons). On the basis of these arguments we can draw a schematic energy band diagram as given in Figure 3.

Looking at the S vs. T^{-1} variation, particularly the linear parts of the curve, one can guess about the conduction mechanism. The conduction can be extrinsic or intrinsic. Let it be extrinsic and the charge carriers localized at impurity centers. The two possible conduction mechanisms then will be either hopping of charge carriers from impurity centers to normal lattice sites or conduction via band mechanism by ionization of the impurity centers to conduction or valence band. In the former case (hopping conduction), S values are expected to be high (~ 0.5 mV K^{-1}) and independent of temperature. In the latter case (band conduction), S values are again expected to be high with the S vs. T^{-1} plot giving the same slope as the log σ vs. T^{-1} plot for one type of impurity. The S data do not agree with either of these expectations. This rules out extrinsic conduction in the studied temperature range. Intrinsic conduction in these solids again can be of hopping or band type. However, the small values of S exclude d band hopping conduction. Thus intrinsic energy band conduction seems to be the mechanism which can explain our data. The four relevant bands for this purpose have been stated above. The choice of the conduction band can be done on the basis of our experimental data.

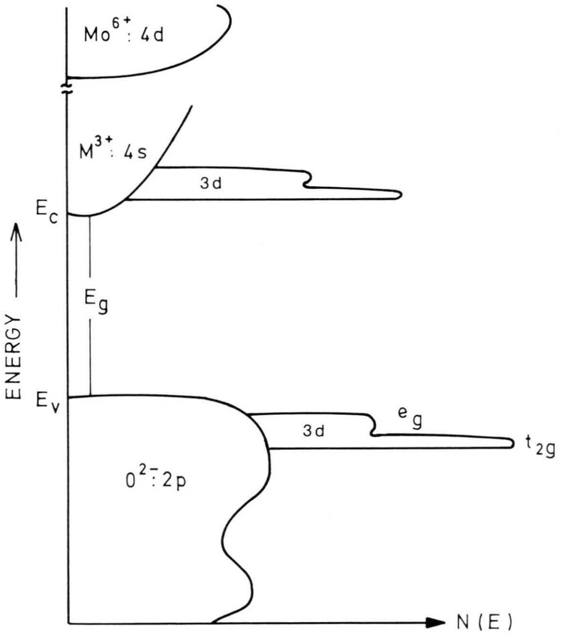

Fig. 3. Schematic energy band diagram for the studied molybdates. The relative positions of the bands may change in different molybdates. (Please read for 3d in the upper part M^{2+}: 3d and in the lower part M^{3+}: 3d.)

Let the conduction process involve O^{2-}:2p as valence band and M^{3+}:3d as conduction band. In view of the fact that 3d bands are not expected to support metallic conduction, the slope of the S vs. T^{-1} plot is expected to be the same as that of the log σ vs. T^{-1} plot. Besides this, S values are expected to be high. But this is not the case for our S data. The small values of S and the very

Table 3. Electrical transport parameters of studied molybdates.

	E_g (eV)	Charge carrier mobility					
		μ_e			μ_h		
		Below phase transition temperature					
		$\mu_e\,(\mathrm{m^2\,V^{-1}\,s^{-1}}) \times 10^4$			$\mu_h\,(\mathrm{m^2\,V^{-1}\,s^{-1}}) \times 10^4$		
		500 K	600 K	700 K	500 K	600 K	700 K
$Cr_2(MoO_4)_3$	2.40	7.23	3.27	1.85	1.34	0.61	0.34
$Ni_2(MoO_4)_3$	2.36	3.36	1.51	0.83	0.56	0.25	0.14
		Above phase transition temperature					
		$\mu_e\,(\mathrm{m^2\,V^{-1}\,s^{-1}})$			$\mu_h\,(\mathrm{m^2\,V^{-1}\,s^{-1}})$		
$Cr_2(MoO_4)_3$	2.82	0.372	0.226	0.180	0.360	0.219	0.175
$Ni_2(MoO_4)_3$	2.82	0.295	0.198	0.143	0.286	0.192	0.139

small slope of the S vs. T^{-1} plot indicate that the involved valence and conduction bands are quite wide with charge carrier mobilities of almost equal order in both the bands. This suggests that the conduction process involves O^{2-}:2p as valence and M^{3+}:4s as conduction band. The schematic energy band diagram for these solids then becomes as shown in Figure 3. Both solids are ionic compounds as indicated by our susceptibility data [5, 7]. Thus polaron formation in the bands is not ruled out. The polarons are expected to be large with intermediate coupling, where the mobility will vary with temperature according to relation

$$\mu = \mu_0 \exp\{-\hbar w_0/k T\}, \qquad (3)$$

where w_0 is the longitudinal optical mode frequency of the solid. Using general expression for $n_e (= n_h)$ according to normal band theory one can obtain expressions for σ and S [13]. Employing the procedure as detailed in earlier publications [9, 10, 13] of our group, values of E_g, μ_e and μ_h at different temperatures are obtained as given in Table 3. Here it has been assumed that $m_e^* = m_h^* = m_e$ (free electron mass), and that the temperature variations of m_e^*, m_h^* and μ_e, μ_h are similar. The evaluated values of μ_e and μ_h are quite appropriate for band conduction.

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